X-ray induced modification of electronic properties of boron nitride thin films

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X-ray induced modification of the electronic properties of nanocrystalline boron nitride (BN) films with different compositions and carbon impurity contents is reported. The related changes of the surface composition and valence band structures of the irradiated films are discussed. X-ray irradiation of nanocrystalline BN films is shown to widen areas with intermediate values of electroconductivity (associated with areas of high emission density) and to increase the average value of electroconductivity by redistributing surface potentials and electron emission sites. Improvement of the field emission is observed with both increasing electron current and diminishing thresholds. Longer x-ray irradiation times yield greater improvement. © *2000 American Institute of Physics.* [S0021-8979(00)03621-5]

INTRODUCTION

Boron nitride (BN) has recently emerged as a promising material for the development of a more effective class of thin-film field electron emitters. BN is chemically, thermally, and mechanically stable and exhibits a negative electron affinity (NEA) that is recognized as a favorable factor for electron field emission. NEA in BN thin films and bulk crystals was observed by ultraviolet photoemission spectroscopy in 1958.[1] NEA is also seen on hydrogen-terminated polycrystalline *c*-BN grown by high-pressure high-temperature synthesis.[2] Nevertheless, the presence of NEA is far from being a sufficient condition for effective electron emission. Recently, we have shown that the effects of (i) inhomogeneity of the surface relief and electroconductivity distribution, (ii) deviations from stoichiometric composition, and (iii) the presence of impurity atoms, strongly influence the emission properties of BN films.[3]

Pryor reported electron emission from carbon-doped boron nitride in 1996, but did not explain the observed low emission threshold.[4,5]

Our previous studies have demonstrated good emission properties of BN films grown by ion- and plasma-source assisted physical vapor deposition. Stable emission currents were observed under threshold fields of 20–30 V/μm, with electron emission densities over 1 A/cm^2. One way to improve emission characteristics is by changing the film surface structure by means of different postgrowth surface modification processes. We have already shown this in our previous works on UV laser-induced modification of diamond[6] and carbon nitride[7] films. Also, in our previous work on the laser photoconductivity (PC) of boron nitride films, we reported that x-ray irradiation of BN thin films can significantly improve the PC signal by generating additional energy levels in the band gap.[8] Similarly, it is reasonable to assume that the increased carrier density might facilitate the field electron emission, which requires that sufficient electrons be transported to the conduction band through the thin film surface.

In the present work, we report results from the x-ray induced modification of electronic properties of BN films with different compositions and carbon impurity contents.

EXPERIMENTS

Prior to deposition, high conductivity silicon (100 *n*-type) substrates were degreased using standard solvents, rinsed in de-ionized water and dried with nitrogen. The substrates were also cleaned *in situ* under argon bombardment for 10 min.

BN thin films (30–100 nm thickness) were grown in a high vacuum reactor equipped with an Auger spectrometer. High purity boron was evaporated by electron-beams and deposited at a rate of 0.2 Å/s, as controlled by a quartz crystal monitor. Both End-Hall ion (Mark II) and electron cyclotron resonance (ECR)–ASTEX plasma sources were used for nitrogen species delivery. The ion beam energy and current in the End-Hall ion source were fixed at 45 eV and 110 mA. The N_2 flow through the ECR source varied from 2 to 5 sccm, and the power of the ECR was maintained at 75 W. The growth temperatures ranged from 80 to 450 °C. The pressure during deposition was 10^{-5} and 10^{-4} Torr using End-Hall and ECR plasma sources, respectively. *In situ* Auger electron spectroscopy measurements were performed to check the cleanliness of the substrates prior to deposition and to determine the postgrowth surface composition.

The BN films were irradiated with 1 kW Cu $K\alpha$ x rays in vacuum over varying exposure times. The field emission characteristics of the films were studied in a high vacuum chamber with a pressure below 10^{-7} Torr. Four tungsten tip probes (anodes) with 20 μm curvature radii were placed at a distance of 10–100 μm from the sample surface (cathode).

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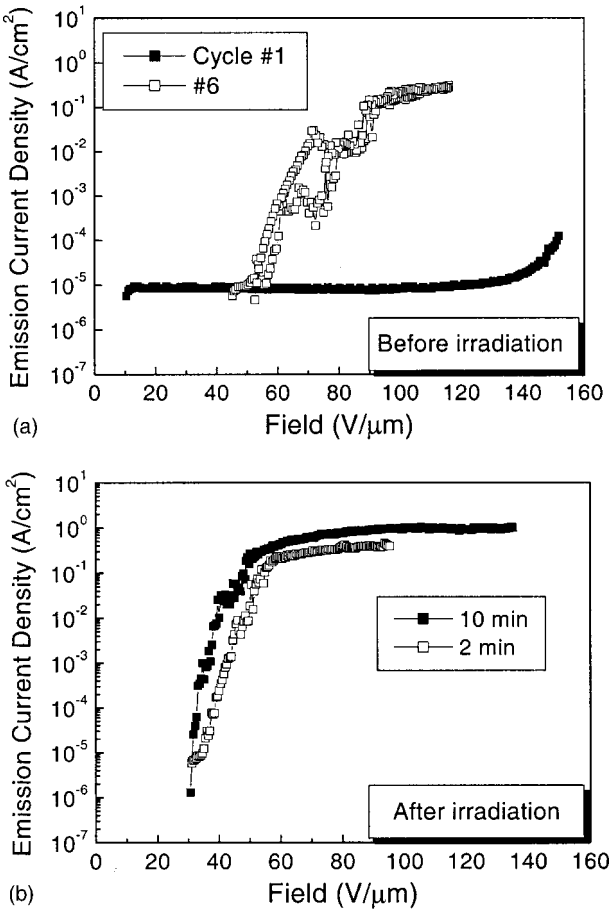

FIG. 1. Electron field emission of BN film before (a) and after (b) x-ray irradiation.

dc voltages up to 8 kV were applied between the sample and each probe separately to induce field emission. The measurement procedure included recording the emission current during the automated increasing-decreasing cycles of the electrical field. The emission current density was calculated by dividing the measured current by the total surface area of the four tips used.

The correlation between the surface relief, electron field emission, and surface electroconductivity of the BN thin films was performed using scanning tunneling field emission microscopy. This mapping technique is based on recording the electron current through the vacuum gap between the sample surface and the probe at a stable applied voltage. It can operate in different modes with a spatial resolution of a few nanometers and allows the generation of maps of the surface topography, electron emission, and surface potential distribution (surface electroconductivity). The comparison of the ''relief,'' ''emission,'' and ''surface potential'' maps permits correlating the topography, field electron emission, and conduction properties of the sample surface.

The surface electronic structure, surface composition, and the valence band characteristics were investigated using x-ray photoelectron spectroscopy (ESCALab-5, VG, England) with Al $K\alpha$ monochromized radiation (1486.6 eV, with a photoelectron energy resolution of 0.6 eV). The density of states distributions was obtained after subtracting the

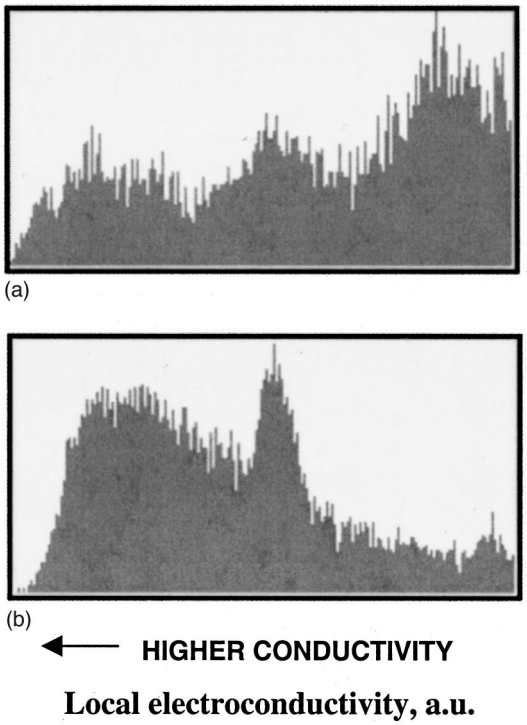

FIG. 2. Typical histograms of surface electroconductivity value distribution in BN film before (a) and after (b) x-ray irradiation. The analysis was made over an area of 20×20 μm^2.

background counts. For the energy scale calibration, we used the position of the Au $4f_{7/2}$ peak (83.8 eV) as a reference. The characteristic peaks corresponding to B–N bonds were associated with well-known energies from studies of the electronic structure of boron nitride.[9] For additional control, our data were compared with *h*-BN and *c*-BN valence band structure calculations.[10–12] Thus, the zero energy was unequivocally fixed at the Fermi level position under the empty band approximation.

RESULTS AND DISCUSSION

A series of BN thin films was irradiated with x rays over different exposure times (2 and 10 min), and the changes in electron field emission were measured. Typical emission characteristics of the thin films before and after the x-ray irradiation are presented in Fig. 1. In all cases one can see a significant lowering of the emission threshold after the x-ray exposure. However, the effect is higher after 10 min exposure time. A minimum field emission threshold and stable emission characteristics were achieved only after a series of loading cycles, which implies that a substantial modification

TABLE I. Quantitative XPS surface analysis of two BN samples as deposited before and after x-ray irradiation.

	N/B		C%		O%	
Sample No.	I	II	I	II	I	II
Original	1.12	1.19	5	6	5	6
2 min x ray	1.02	1.16	2	4	2	4
10 min x ray	0.95	1.05	1	1.5	1	1.5

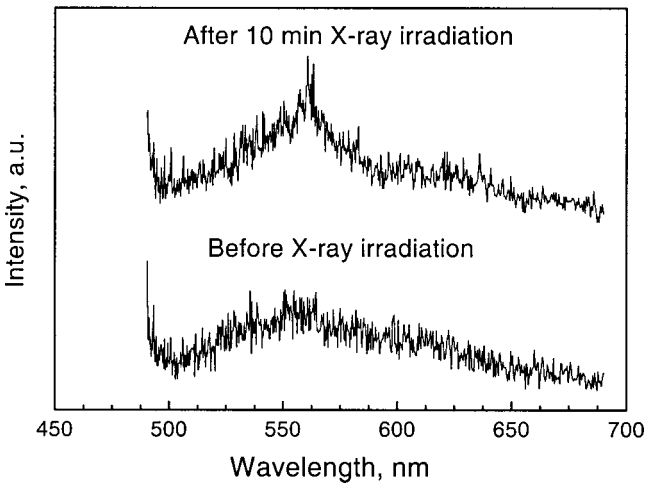

FIG. 3. Typical luminescence of BN film before and after x-ray irradiation.

of the surface structure is necessary to produce high emission current at low applied field. In the first cycle, substantial electron emission is obtained only under higher voltage thresholds.

The surface potential/emission mapping shows that at least three distinct phases—a conductive phase, a quasidielectric phase, and an intermediate phase—can be distinguished from the histogram representing the distribution of the surface electroconductivity (Fig. 2).

The main effect induced by x-ray irradiation is the redistribution of these areas and the increase of the average electroconductivity. In particular, the fraction of the intermediate phase is increased. According to the maps of surface electroconductivity and field emission distributions we obtained,[3] this phase is usually associated with areas of high emission density. Thus, the active emission region widens after the x-ray exposure. Study of Fourier spectra of the electroconductivity distribution maps also revealed the increase of the characteristic inhomogeneity size—from nanometer to micrometer scale.

The results of quantitative x-ray photoelectron spectroscopy (XPS) surface analysis of two BN samples are presented in Table I. After x-ray irradiation, excess nitrogen, oxygen, and carbon are reduced on the surface. We assumed here that the process of surface cleaning was taking place due to x-ray exposure.

To further understand the x-ray effect on thin film electronic structure, XPS studies were performed on the valence band structure of typical BN thin films. These measurements demonstrate a distinct postirradiation difference in the location of electronic states in the effective band gap of the thin films. In particular, the top of the valence band is shifted versus the position of the Fermi layer about 0.2 eV in most cases. This situation is similar to that observed in our previous studies of x-ray induced enhancement of laser multiphoton photoconductivity in BN films.[8]

The luminescence spectra of as-grown and x-ray irradiated films were studied at liquid nitrogen temperature (see Fig. 3). One can see the enhancement of the wide band around 560 nm. The corresponding quantum energy is 2.2 eV. We attribute this effect to x-ray induced changes in the BN film electronic state energy distribution, probably the generation of additional permitted energy levels in the band gap, which does not contradict the observed changes in the distribution of valence band density of states.

CONCLUSION

X-ray irradiation of boron nitride thin films significantly modifies their surface electronic structure and composition. It also improves the electron field emission characteristics of the thin films, both increasing current and lowering the threshold. Longer irradiation times yield greater improvements. We believe that two major mechanisms are responsible for the emission enhancement.

(i) Irradiation produces defects in the film which increase carrier density by creating additional donor/acceptor levels. This effect promotes efficient electron transport from the bulk to the film surface, which is necessary for high emission currents. The appearance of these defects is confirmed by the study of the BN films' luminescence spectra, and is supported by the difference in the density of states distribution near the valence band edge.

(ii) X rays remove impurity atoms from the surface layer of the irradiated film which changes the surface electroconductivity distribution. This alters the ratios of the three distinct surface phases detected by surface mapping, increasing the area of the intermediate ''semiconducting'' phase that coincides with the region of maximum emission intensity. This undoubtedly plays an important role in enhancing the prebreakdown electron emission of the films. The observed increase of the scale of surface inhomogeneity is still not understood, but it could be connected to the surface cleaning effect under x-ray exposure

The current results are an important step towards developing reliable methods of postgrowth modification of BN coatings for electronic and optoelectronic applications. We also believe that the x-ray effect is fundamental in understanding the basic mechanism of the field emission process. Finally, it could be a means to easily activate electron field emitter materials.

ACKNOWLEDGMENTS

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[1] M. J. Powers, M. C. Benjamin, L. M. Porter, R. J. Nemanich, and R. F. Davis, Appl. Phys. Lett. **67**, 3912 (1995).
[2] K. P. Loh, M. Nishitani-Gamo, T. Sakaguchi, T. Taniguchi, and T. Ando, Appl. Phys. Lett. **72**, 3023 (1998).
[3] N. Badi *et al.*, J. Vac. Sci. Technol. A **17**, 1191 (1999).
[4] R. W. Pryor, Appl. Phys. Lett. **68**, 1802 (1996).

[5] R. W. Pryor, Mater. Res. Soc. Symp. Proc. **416**, 425 (1996).
[6] M. V. Ugarov, V. P. Ageev, A. V. Karabutov, E. N. Loubnin, S. M. Pimenov, V. I. Konov, and A. Bensaoula, J. Appl. Phys. **85**, 8436 (1999).
[7] N. Badi, A. Bensaoula, V. Ageev, A. Karabutov, M. Ugarov, and E. Loubnin, J. Appl. Phys. **88**, 7346 (2000).
[8] V. P. Ageev, S. Klimentov, M. Ugarov, E. Loubnin, A. Bensaoula, N. Badi, A. Tempez, and D. Starikov, Appl. Surf. Sci. **138–139**, 364 (1999).
[9] K. Hamriu and G. Johansen, Phys. Scr. **1**, 227 (1970).
[10] E. Tegeler, N. Kosuch, G. Wirch, and A. Faessler, Phys. Status Solidi B **91**, 223 (1979).
[11] K. Hamriu and G. Johansen, Phys. Scr. **1**, 227 (1970).
[12] V. G. Aleshin, Solid State Commun. **19**, 903 (1976).